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Evaluation of Proton-Ligand Dissociation Constant of 1-(2-(1-(2-Hydroxyphenyl) Ethylidene) Hydrazono)-1-Phenylpropan-2-One and Formation Constants of its Complexes with Cobalt, Nickel and Copper in Dioxane-Water System by Potentiometry.

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Abstract: ***A ligand 1-(2-(1-(2-hydroxyphenyl) ethylidene) hydrazono)-1-phenylpropan-2-one oxime (HHPEHPPO) has been synthesized. Interest in this ligand was due to the ambidenticity as well as probable multidenticity in coordination with metal ions of the transition element series. The ligands have two probable dissociable protons, yet our studies reveal that it is monobasic in nature. The proton ligand dissociation constant of HHPEHPPO and the stability constants of its complexes with cobalt, nickel and copper have been determined potentiometrically by Calvin-Bjerrum potentiometric technique as modified by Irving and Rassotti in KCL and 60:40(V/V) 1,4-dioxane - water system at room temperature in an inert, nitrogen atmosphere at variable ionic strengths. The complex formation occurs in a stepwise manner and the stepwise (ML^+ and ML_2) formation constants of the complexes species increases in the order of Co^{2+}, Ni^{2+} and Cu^{2+} for both the species. The most stable species being ML_2.***
Key Words: - Stability constants, Stepwise formation Constants, Ionic Strength, Metal ion Complexes, organic ligand, Potentiometry.

I. INTRODUCTION

Coordination complexes of oximino ketones and their derivatives have attracted great attention over the past decades due not only to their facile syntheses and the accessibility of diverse structural modifications, but also to their wide application in analytical [1], bioinorganic system [2], catalyst [3,4], medicine[5,6] etc. This is primarily because of the various positions of probable donor atoms, presence of >C=N-group (biologically important group as it shows microbial activity) and inherent ambidentate character of the ligand. As such, these ligands are known to report metal complexes of varied geometries, stabilities and applications.

A survey of the literature shows that no study on the proton dissociation constant of the above mentioned organic ligand and stability constants of its metal complexes has been done so far. In the present study we are therefore reporting the effect of varying ionic strength on the dissociation constant and stability constants of Co^{2+}, Ni^{2+} and Cu^{2+} complexes of the said organic ligand.

II. EXPERIMENTAL

All chemicals used were of AR grade. Other chemicals if used were purified by standard methods before use. The organic solvents used were purified by standard methods. Carbonate free bid stilled water was prepared by standard method prescribed by Vogel. Volumetric glass wares were calibrated before use.

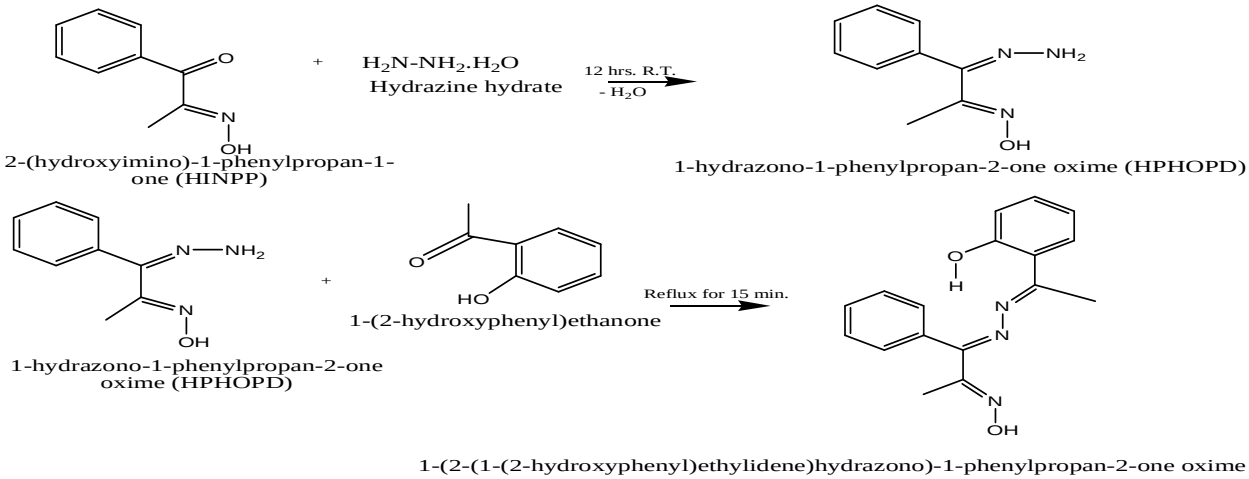
An Equiptronics pH-meter (EQ-610, accuracy ±0.01unit) with an inbuilt magnetic stirrer was used for the titrations. It was calibrated using buffer solution of pH 4.0, 7.0 and 9.2 prepared using buffer tablets (A.R.). The pH measurements were performed using combined glass electrode. The pH meter readings in the non-aqueous medium were corrected [8].

All the titrations were carried out in a thermostat at room temperature in an inert atmosphere by bubbling nitrogen gas through the solution. This served to maintain an inert atmosphere as well as to stir the solution during titration.

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A. Ligand synthesis (HHPEHPPO)



HPHOPD was synthesized by the method reported by R. G. Deshmukh and N.V. Thakkar [5]. HHPEHPPO was prepared by refluxing a mixture of 0.05 mole of hydrazones derivative of HINPP (HPHOPD**)** and 0.05 mole of 2-hydroxyacetophenone in 50.0 cm^3ethanol for 15 minutes. Completion of reaction was confirmed by TLC. The yellow solid product formed, was filtered, washed thoroughly with water and dried in oven at 110^0C. It was recrystallized from ethanol and analyzed for C, H, and N.

B. Potentiometric measurements

A ligand solution (0.05mol·dm^{-3}) was prepared by dissolving an accurately weighed amount of the solid in dioxane (A.R.). Metal ion solutions (0.01mol·dm^{-3}) were prepared using the corresponding metal chlorides in bid stilled water and standardized by titrating with E.D.T.A. [7]. Solutions of 0.01mol·dm^{-3} HCl and 1.0 mol·dm^{-3} KCl were also prepared in bid stilled water. A carbonate-free potassium hydroxide solution in 60% Dioxane-water mixture (by volume) was standardized using a standard solution of succinic acid and used as titrant. The following mixtures were prepared and titrated potentiometrically at R.T. i.e. 301 K against standard 0.1 mol·dm^{-3} KOH in a 60% (by volume) Dioxane-water mixture:

1) 5.0 $cm^3$0.10 mol·dm^{-3}HCl + 30.0 cm^3Dioxane.
2) 5.0 $cm^3$0.10 mol·dm^{-3}HCl +5.0 $cm^3$0.05 mol.dm^{-3}ligand + 25.0 cm^3 Dioxane.
3) 5.0 cm^3 0.10 mol·dm^{-3} HCl + 5.0 $cm^3$0.05 mol.dm^{-3} ligand +5.0 $cm^3$0.01 mol.dm^{-3} metal chloride + 25.0 cm^3 Dioxane.

In each case an appropriate volume of 1.0 M KCl was added to maintain 0.05 mol.dm^{-3} ionic strength and the total volume was made up to 50.0 cm^3 with bidistilled water and titrated against standardized 0.10 mol.dm^{-3} potassium hydroxide solution till precipitation starts or constant pH values observed, whichever early. Similar titrations were carried out for ionic strength of 0.075 mol·dm^{-3} and 0.10 mol·dm^{-3}.

III. RESULTS AND DISCUSSION

A. Ligand (HHPEHPPO) characterization

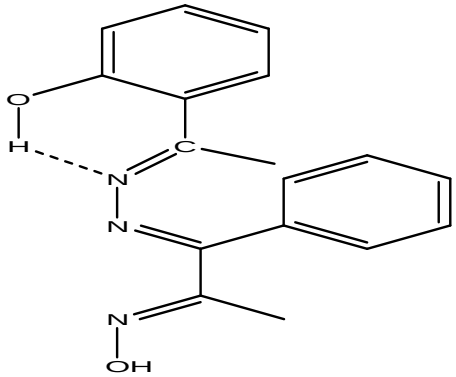


Fig.1

Characterization of the ligand is done by using analytical data obtained from FTIR, PMR, UV-VISIBLE spectroscopy, GC-MS, elemental analysis etc. The molecular weight of ligand is 295gmol^{-1} determined by GC-MS, it melts at 203^0C. It is yellow crystalline solid, soluble in chloroform, acetone, DMF, DMSO, dioxane, dilute alkali etc. and is partially soluble in methanol and ethanol.

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B. Calculations And Conclusions

The average number of the protons associated with ligand at different pH values, $\overline{n_A}$ was calculated from the titration curves of the acid in the absence and presence of ligand from equation (1)

$$\overline{n_A} = Y - \frac{(V_2 - V_1)(N^0 + E^0)}{(V^0 + V_1)TC_L^0} \quad (1)$$

where Y is the number of ionizable proton(s) in ligand (Y = 1) and $V1$and $V2$are the volumes of alkali required to reach the same pH on the titration curve of hydrochloric acid and reagent, respectively, $V0$ is the initial volume (50.0 cm3) of the mixture, TC_L^0 is the total concentration of the reagent (ligand), $N0$ is the normality of potassium hydroxide solution, and $E0$ is the initial concentration of the free acid. Thus, the formation curves ($\overline{n_A}$ versus pH) for the proton-ligand systems were constructed and found to extend between 0 and 1 in the $\overline{n_A}$ scale. This means that ligand has one ionizable proton. The formation curves for the metal complexes were obtained by plotting the average number of ligands attached per metal ion ($\bar{n}$) versus the free ligands exponent (pL), according to Irving and Rossotti [8]. The average number of the reagent molecules attached per metal ion ($\bar{n}$), and free ligands exponent, pL, can be calculated using (2) and (3) respectively:

$$\bar{n} = \frac{(V_3 - V_2)(N^0 + E^0)}{(V^0 + V_2)\overline{n_A}TC_M^0} \quad (2)$$

$$pL = \log_{10}\left[\frac{\sum_{n=0}^{n=j}\beta_n^H (1/anti\log pH)^n}{TC_L^0 - \bar{n}TC_M^0} * \frac{(V^0 + V_3)}{V^0}\right] \quad (3)$$

Where, TC_M^0 is the total concentration of the metal ion present in the solution and β_n^H is the overall proton-reagent stability constant. V_1, V_2, and $V_3$are the volumes of alkali required to reach the same pH on the titration curves of hydrochloric acid, organic ligand, and complex, respectively. These curves were analyzed, and the successive metal-ligand stability constants were determined. The values of the stability constants ($\log K_1$and $\log K_2$) are given in Tables 2, 3 and 4. The following general remarks can be pointed out.

1) The maximum value of $\bar{n}$ was ~2 indicating the formation of 1:1 and 1:2 (metal: ligand) complexes only [9].

2) The metal ion solution used in the present study was very dilute (1×10^{-3}mol·dm^{-3}); hence there was no possibility of formation of polynuclear complexes [10, 11].

3) The metal titration curves were displaced to the right hand side of the ligand titration curves along the volume axis, indicating proton release upon complex formation of the metal ion with the ligand. The large decrease in pH for the metal titration curves relative to ligand titration curves points to the formation of strong metal complexes [12, 13].

4) For the same ligand at constant temperature, the stability of the chelates increases in the order Co^{2+}, Ni^{2+}, and Cu^{2+}[14, 15]. This order largely reflects that the stability of Cu^{2+}complexes is considerably larger than those of other metals of the 3d series. Under the influence of both the polarizing ability of the metal ion and the ligand field Cu^{2+}will receive some extra stabilization due to tetragonal distortion of octahedral symmetry in its complexes. The greater stability of Cu^{2+}complexes may be due to the *Jahn-Teller* effect which distorts the regular octahedron environment for the metal ion.

The dissociation constant (pK_H) for ligand, as well as the stability constants of its complexes with Co^{2+}, Ni^{2+}, and Cu^{2+}, have been evaluated at 0.05mol·dm^{-3},0.075mol·dm^{-3} and 0.1mol·dm^{-3}, and is given in Tables 1-4.

Table-1: Proton –ligand dissociation constants at R.T. (301K):

Sr. No.	Ionic Strength	Proton-Ligand Constants		
		By half integral method	By graphical method	pK_H
1	0.05	10.80	10.80	10.80
2	0.075	10.71	10.70	10.70
3	0.1	10.63	10.62	10.62

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Table-2: Stepwise stability constants for ML^+ and ML_2 complexes in 60:40 (by volume) dioxane-water mixture and I = 0.05 $moldm^{-3}$ at room temperature (301K):

M^{n+}	Logk1		Logk2		Logβ= logk1 + logk2
	By graph	By calculations	By graph	By calculations	
Co^{2+}	9.45	9.45	7.05	7.04	16.50
Ni^{2+}	9.91	9.92	7.41	7.41	17.33
Cu^{2+}	10.46	10.45	9.56	9.54	20.00

Table-3: Stepwise stability constants for ML^+ and ML_2 complexes in 60:40 (by volume) dioxane-water mixture and I = 0.075$moldm^{-3}$ at room temperature (301K):

M^{n+}	Logk1		Logk2		Logβ= logk1 + logk2
	By graph	By calculations	By graph	By calculations	
Co^{2+}	9.43	9.42	6.90	6.91	16.32
Ni^{2+}	9.82	9.83	7.33	7.33	17.16
Cu^{2+}	10.43	10.42	9.44	9.42	19.85

Table-4: Stepwise stability constants for ML^+ and ML_2 complexes in 60:40 (by volume) dioxane-water mixture and I = 0.1$moldm^{-3}$ at room temperature (301K):

M^{n+}	Logk1		Logk2		Logβ= logk1 + logk2
	By graph	By calculations	By graph	By calculations	
Co^{2+}	9.32	9.32	6.83	6.84	16.15
Ni^{2+}	9.76	9.75	7.23	7.21	16.97
Cu^{2+}	10.38	10.38	9.35	9.35	19.73

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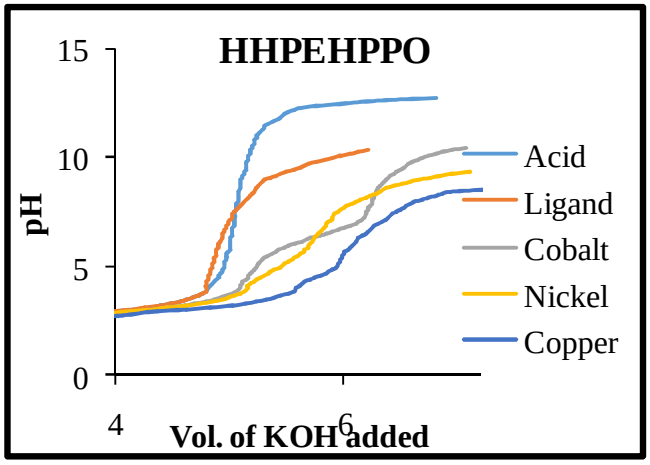


Figure:2 Acid, ligand and metal ions titration curves

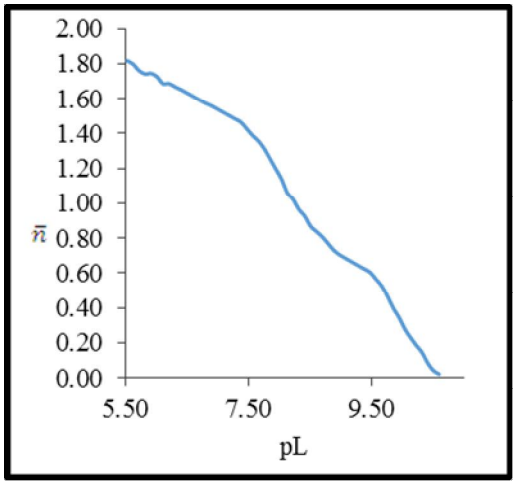


Figure: 3 Complex formation Curve

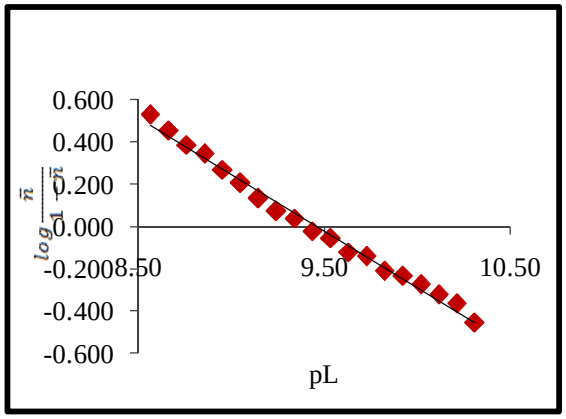


Figure: 4 Linear plots for evaluation of $\log K_1$

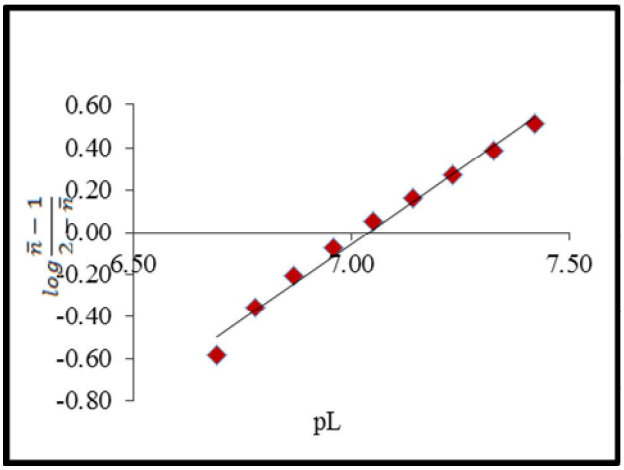


Figure: 5 Linear plots for evaluation of $\log K_2$

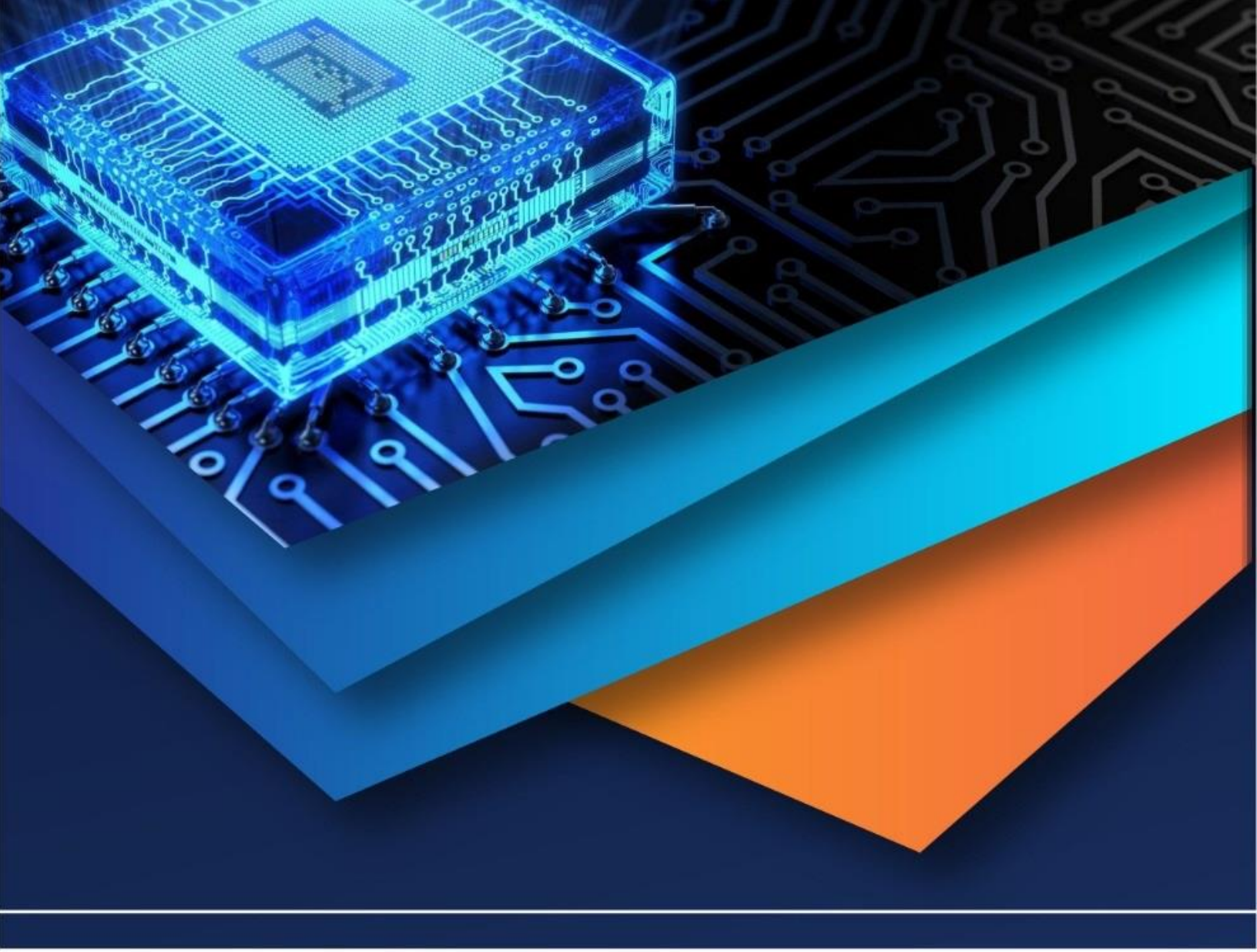
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